

**KINETIC STUDY OF
SODIUM SULFIDE-CARBON DIOXIDE-WATER SYSTEM
IN A LAMINAR JET**

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A Thesis Submitted
In Partial Fulfilment of the Requirements
for the Degree of
MASTER OF TECHNOLOGY

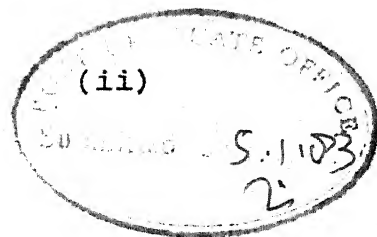
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NOMENCLATURE

- A^* equilibrium concentration of dissolved carbon dioxide at interface (gmol/cm^3)
 B^0 concentration of B (hydroxyl ion) in the bulk liquid (gmol/cm^3)
 c concentration of ion in solution (gion/cm^3)
 D_A diffusivity of carbon dioxide (cm^2/s)
 E enhancement factor, i.e. factor by which amount of A(gas) absorbed in time t is increased by reaction (dimensionless)
 E_i instantaneous enhancement factor (dimensionless)
 h length of jet (cm)
 h_i solubility factor for electrolytes of i species (litre/gmol)
 h_+, h_- contributions of positive ion, negative ion, and gas to solubility factor h (litre/gmol)
 I_i ionic strength for i species = $\frac{1}{2} \sum c_i z_i^2$ (gion/litre)
 H Henry's law constant in electrolyte ($\text{atm cm}^3/\text{gmol}$)
 H_w Henry's law constant in water ($\text{atm cm}^3/\text{gmol}$)
 k_2 second-order rate constant for reaction of A (litre/gmol s)
 M $\frac{k_2 B^0 t}{4}$ (dimensionless)
 q total rate of absorption in laminar jet apparatus (gmol/s)
 Q amount of gas absorbed by per unit area in time t (gmol/cm^2)
 t contact time (s)

| | |
|---------|--|
| T | temperature ($^{\circ}\text{C}$ or $^{\circ}\text{K}$) |
| v | liquid flow rate (cm^3/s) |
| z | stoichiometric factor (dimensionless) |
| z_i | valencies of ions |
| μ | viscosity of liquid (cp) |
| μ_w | viscosity of water (cp) |

ABSTRACT

The kinetics of absorption of carbon dioxide in alkaline solutions containing sodium sulphide have been studied. The absorption rates of carbon dioxide in a laminar jet have been measured at different temperatures. The absorption of carbon dioxide in the liquid can be regarded as a diffusion process accompanied by a fast pseudo-first order reaction since the contact time is very short and of the order of 25×10^{-3} s. The reaction rate constant, k_2 , of the reaction $\text{CO}_2 + \text{OH}^- \rightarrow \text{HCO}_3^-$ has been measured for sodium sulphide solutions in the concentration range of 0.05 to 0.212 M over the temperature of 19 to 32°C. Effect of various electrolytes such as sodium chloride and sodium sulphate has also been studied and it is found that the rate constant, k_2 , increases with increase in ionic strength of electrolyte. The activation energy of the reaction is found to be of the order of 12.572 kcal/gmol.

CHAPTER 1

INTRODUCTION

The kinetics of absorption of gaseous solutes in liquids with chemical reaction is important in the design of gas-liquid contact equipment for process applications and air pollution control devices in chemical and allied industries.

Absorption of carbon dioxide in alkaline solutions is important in chemical recovery operations as in paper mills. Green liquor from sulphate-sulphite cross chemical recovery operations containing sodium carbonate and sodium sulphide is carbonated in two stages to release hydrogen sulphide which is subsequently oxidized and used in making sulphite pulping liquor. In the first stage green liquor is precarbonated by flue gas to a pH of about 9.5. Pre-carbonation upto a pH of 9.5 can also be used for the removal of 80-90 per cent of the silica from green liquor in bamboo- or bagasse - based paper mills.

Kraft green liquor contains

NaOH (8-40), Na_2CO_3 (95-150),

Na_2S (18-25), Na_2SO_4 (0.5-10)

and SiO_2 (0.1 - 15 g/litre).

Absorption of carbon dioxide from flue gas in green liquor is a heterogeneous diffusion process accompanied by chemical reactions in the liquid phase. Mass-transfer and kinetic parameters for the absorption of carbon dioxide into simpler systems such as NaOH and $\text{Na}_2\text{CO}_3 - \text{NaHCO}_3$ are well established. The rate of absorption of carbon dioxide in alkaline process liquors depends upon hydrodynamic factors such as density, viscosity, liquor rate and equipment geometry as well as on physico-chemical factors such as solubility, diffusivity and the kinetics of the liquid-phase reaction which are influenced by temperature, ionic strength and the nature of electrolytes. The degree of hydrolysis of sulphide and carbonate in green liquor would also influence the rate of carbonation. Mahagaonkar and Veeramani⁽²⁾ studied mass transfer aspects of carbonation of $\text{NaOH} - \text{Na}_2\text{S}$, $\text{NaOH} - \text{Na}_2\text{CO}_3 - \text{Na}_2\text{S}$ and commercial green liquor systems in a stirred cell. Enhancement factors were determined experimentally and compared with estimates based on second order irreversible reaction kinetics. Reaction rate constants reported by Pinsent et al.⁽⁶⁾ for sulphide free solutions and the values obtained in preliminary work with laminar jet apparatus for sulphide solutions were used for the theoretical estimation of enhancement factor.

This study is an extension of Mahagaonkar⁽¹⁾ work and deals mostly with the Kinetic Study of Sodium Sulphide -

Carbon Dioxide - Water system in a laminar jet. Experimentally determined value of kinetic constants will give a better estimate of the enhancement factor for reliable sizing of the absorption units for carbonation.

CHAPTER 2

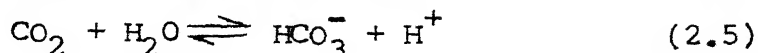
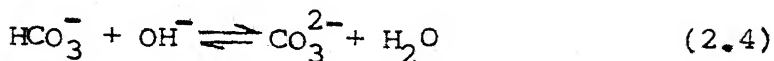
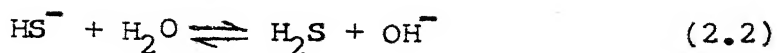
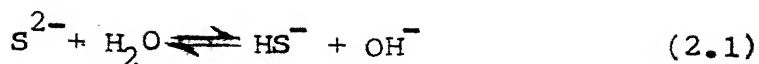
REVIEW OF ABSORPTION STUDIES IN A LAMINAR JET

Laminar jet absorber is very useful for research work as a contacting device since the experimental parameters-contact time, interfacial area, and absorption rate can be closely defined and accurately measured. Measurements of rates of gas-absorption can be used to determine - reaction rate constants for reactions of dissolved gases, diffusivities of gases in solutions and solubilities of gases in liquids with which they react.

In a laminar jet a liquid jet with flat velocity profile enters the gas-space through a circular hole and leaves through a slightly larger hole. The time of exposure to the gas of each element of its surface is the length of the jet divided by its velocity. If one measures the rate of absorption of gas into the jet, one can calculate the amount of gas absorbed by unit area of surface in contact time t . A review of the past work is outlined in the following sections.

2.1 Absorption of Carbon Dioxide into Alkaline Solutions:

Absorption of carbon dioxide into alkaline solutions containing sodium sulphide is accompanied by the following reactions:



In the above reactions it is assumed that sodium sulphide undergoes complete hydrolysis in one step. Reaction (2.1) represents the hydrolysis of sulphide. The hydrolysis of sulphide depends upon pH, temperature and concentration. When pH is above 10.0 reactions (2.1) and (2.2) are shifted towards the left while reaction (2.3) is displaced towards the right and followed by reaction (2.4). The second order rate constant for the reaction (2.3) at 20°C and infinite dilution is about 6000 litre/gmol s. The rate constant depends upon temperature, ionic strength and nature of electrolytes.⁽⁴⁾ Direct hydration of carbon dioxide according to reaction (2.5) is first order, with a rate constant of about 0.02 s⁻¹ at 20°C. Thus in any solution in which the concentration of hydroxyl ion is greater than 10⁻⁴ gion/litre (corresponding to a pH of 10.0), the rate of reaction of carbon dioxide by reaction (2.3) will be greater than 0.6 s⁻¹ and thus more than 30 times as fast as its reaction by (2.5). Therefore, when the pH is above 10.0, reaction (2.3) can be considered to be the dominant over the pH range of 10-14.

Reaction (2.5) becomes increasingly important as the pH decreases below 10.0.

2.2 Mass Transfer Aspects and Kinetics of Absorption of Carbon Dioxide into Alkaline Solutions:

Laminar jet has been used by several investigators for the mass transfer and kinetic studies. The experimental conditions and the results obtained by various workers are given in Table 2.1. It is always advisable to test the laminar jet system for satisfactory behaviour by absorbing carbon dioxide in water. The solubility and diffusivity of carbon dioxide is well established and Table 2.2 gives the solubility and diffusivity of carbon dioxide in water at different temperatures.

In a laminar jet apparatus⁽³⁾ total rate of absorption of gas into the jet, q , and the contact time of the gas with liquid jet, t , is given by equations (2.6) and (2.7).

$$q = \frac{\pi d h q}{t} \quad (2.6)$$

$$t = \frac{h}{u} = \frac{\pi d^2 h}{4v} \quad (2.7)$$

where q = total rate of absorption of gas into the jet (gmol/s)

d = diameter of the jet (cm)

h = length of the jet (cm)

t = contact time (s)

v = liquid flow rate (cm³/s)

u = liquid velocity (cm/s)

TABLE 2.1: LAMINAR JET ABSORBER (7,8) FOR THE ABSORPTION OF CARBON DIOXIDE INTO ALKALINE SOLUTIONS

| System (1) | Temperature °C (2) | Ionic Strength gion/litre (3) | Remarks (4) | Ref. (5) |
|--|--------------------------|-------------------------------------|--|-------------|
| 1. Sodium hydroxide, potassium hydroxide, Lithium hydroxide | 20 | 0 - 3.1 | Kinetic constant values for different ionic strength reported for the three different absorbents | (5) |
| 2. Sodium, Potassium buffers containing arsenite, hypo- chlorite, formal- dehyde | 15-60 | 0 - 5.0 | Absorption rate of carbon dioxide into carbonate buffer containing arsenite, formaldehyde and hypochlorite as catalyst for typical industrial conditions | (12) |
| 3. Sodium hydroxide + Glycerol | 30 | 0 - 1.0 | Kinetics of sodium hydroxide solutions in water-glycerol mixtures by measuring the absorption rate of carbon dioxide. Rate constant found to increase slightly with glycerol-water ratio | (13) |
| 4. Sodium hydroxide | 25 | - | Theoretical rate calculated with a model based on absorption with two second order irreversible reactions. | (14) |

Table 2.1 contd

| (1) | (2) | (3) | (4) | (5) |
|----------------------------------|-----|---------|--|------|
| 5. Sodium carbonate + Glycine | 25 | 0 - 3.0 | Effect of glycine addition on the rate of absorption of carbon dioxide in water, sodium carbonate solutions and sodium carbonate solutions has been determined. The rate of absorption increased to a maximum and then decreased as concentration of glycine increased (0 - 0.6M). | (15) |
| 6. Sodium sulphide | 37 | - | Preliminary study of absorption of carbon dioxide in sodium sulphide solution to complement the data on carbonation of green liquor. | (2) |

TABLE 2.2: SOLUBILITY AND DIFFUSIVITY DATA
FOR CARBON DIOXIDE IN WATER^(4,5)

Total pressure: 1 atm

| Temperature (°C) | Solubility (gmol/litre) | Diffusivity x 10 ⁵ (cm ² /s) |
|---------------------|----------------------------|---|
| 10 | 0.0535 | 1.26 |
| 15 | 0.0455 | 1.45 |
| 19 | 0.0401 | 1.66 |
| 20 | 0.0390 | 1.69 |
| 25 | 0.0335 | 1.94 |
| 27 | 0.0316 | 2.10 |
| 30 | 0.0290 | 2.26 |
| 32 | 0.0274 | 2.32 |

Therefore $Q = \frac{qd}{4v}$ (2.8)

For a purely physical absorption the amount of gas (Q) absorbed by unit area of the surface in time t is given by equation (2.9)

$$Q = 2A^* \left(\frac{D_A t}{A} \right)^{\frac{1}{2}} \quad (2.9)$$

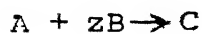
where A^* = solubility of carbon dioxide in non-reacting liquid (gmol/cm³)

D_A = diffusivity of carbon dioxide (cm²/s)

The total rate of absorption of gas in a laminar jet of non-reacting liquid is given by equation (2.10). Equation (2.10) can be derived by combining (2.6), (2.8) and (2.9).

$$q = 4A^* (D_A v h)^{\frac{1}{2}} \quad (2.10)$$

The equation for the absorption of a solute gas which reacts with a component in the quiescent liquid accompanied by pseudo-first order irreversible reaction is given by (2.11). Equation (2.11) is derived by assuming A (dissolved gas) reacting with B (available in liquid) as:



$$Q = A^* (D_A / k_2 B^{\circ})^{\frac{1}{2}} \left((k_2 B^{\circ} t + \frac{1}{2}) \operatorname{erf} (k_2 B^{\circ} t)^{\frac{1}{2}} + \left(\frac{k_2 B^{\circ} t}{\pi} \right)^{\frac{1}{2}} \exp (-k_2 B^{\circ} t) \right) \quad (2.11)$$

where k_2 = second order rate constant (litre/gmol-s)

B° = concentration of B in bulk of liquid (gmol/cm³)

For $k_2 B^0 t \gg 1$ ($k_2 B^0 t > 10$ at least)

$$Q = tA^* (D_A k_2 B^0)^{\frac{1}{2}} \quad (2.12)$$

Equation (2.12) can be used to obtain the value of rate constant, k_2 , in laminar jet apparatus for sodium sulphide solutions.

Enhancement Factor: The factor by which amount of A absorbed in time t is increased by reaction. The enhancement factor, E , for second order irreversible reaction $A + zB \rightarrow C$ is given by equation (2.13).

$$E = \frac{Q}{2A^*} \left(\frac{\pi}{D_A t} \right)^{\frac{1}{2}} = (M(E_i - E)/(E_i - 1))^{\frac{1}{2}} / \tanh(M(E_i - E)/(E_i - 1))^{\frac{1}{2}} \quad (2.13)$$

where $E_i = 1 + \frac{B^0}{zA^*}$ = enhancement factor for instantaneous reaction (dimensionless) (2.14)

z = stoichiometric factor (dimensionless)

$$M = \frac{\pi k_2 B^0 t}{4} \quad (\text{dimensionless}) \quad (2.15)$$

Limiting condition for psuedo-first order reaction is given as

$$(M)^{\frac{1}{2}} \ll E_i \quad (2.16)$$

Equation (2.13) is given in graphical form by van Krevelen⁽¹⁶⁾ and Danckwerts.⁽³⁾ The graph and equations (2.14) and (2.15) can be used for obtaining the theoretical values of enhancement factor, E .

From the foregoing literature survey, it can be observed that kinetic data on the carbonation of alkaline solutions containing sodium sulphide are not available. In order to fill the gap in the literature, the present system sodium sulphide-carbondioxide-water has been taken for kinetic study. In the present study the objective is to obtain the kinetic data of this system and to investigate the effect of important process variables such as temperature, concentration and electrolytes on the rate constant.

CHAPTER 3

EXPERIMENTAL

A laminar jet apparatus was used to obtain the kinetic data for absorption of carbon dioxide into sodium sulphide solution.

3.1 Laminar Jet:

3.1.1 Details of the Apparatus: A sketch of the absorption setup is given in Figure 3.1. A detailed diagram of the laminar jet is shown in Figure 3.2. Laminar jet assembly consisted of a glass chamber made out of a pyrex glass cylinder of 6 cm I.D., flattened and ground at the open top. The nozzle was mounted on the end of a stainless steel slide tube which passed through an 'O' ring seal in the mild steel cover plate, used to seal the top of the glass chamber. The diameter of jet was 0.156 cm. The surface of the cover plate was polished to a fine finish so that a gas-tight seal allowing sliding motion was possible with the aid of stop cock grease. The jet length was adjusted by lowering or raising the slide tube. The jet chamber was provided with a gas inlet, a drain and a thermometer port. The flow nozzle, made of brass, was carefully **turned** to a shape shown in the Figure 3.2 and the profile of the covering section was made as smooth as possible. The throat and face surfaces were

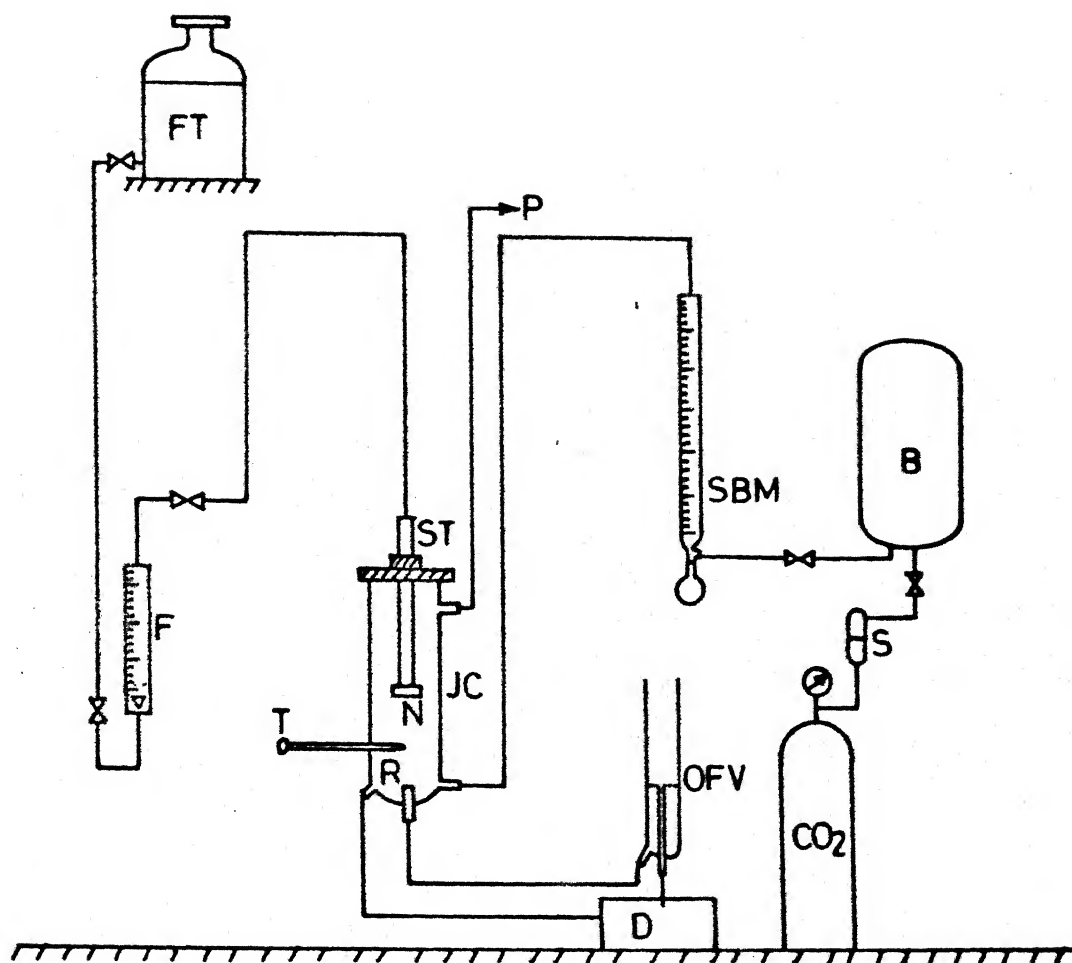


Fig. 3.1 - Laminar jet apparatus. B-CO₂ balloon; D- Drain;
 F-Flowmeter; FT-Feed tank; JC - Jet chamber;
 N-Nozzle; OFV-Overflow vessel; P-Gas purge line;
 R-Receiver; S-Saturator; SBM-Soap bubble meter;
 ST-Slide tube; T-Thermometer.

polished to a smooth finish. A jet of liquid flowed downward from the nozzle through an atmosphere of carbon dioxide into a glass receiver of diameter slightly more than the jet. The receiver was connected to the overflow vessel for the adjustment of liquid level in the receiver. The gas inlet was connected to the soap bubble-flow meter. The nozzle tube was connected to the rotameter.

The gas entered the bottom of a graduated tube through a slide arm. The bottom of the tube contained soap or detergent solutions; the level of this solution was raised by squeezing the rubber bulb so that the solution momentarily covered the gas inlet. This caused a film to form and moved up the tube. The rate of movement of the film was exactly equal to the rate of flow of gas and was determined by a stop watch. The soap bubble meter was connected to the rubber balloon to ensure the flow of carbon dioxide.

The balloon was made from an unstretched rubber. Carbon dioxide was stored in the balloon from the saturator at atmospheric pressure.

The saturator was connected to the carbon dioxide cylinder. Carbon dioxide was passed through the saturator containing water vapour to saturate the gas-stream. It was done by bubbling the gas through water.

3.1.2 Procedure: During operation deaerated liquid flowed from an overhead tank by gravity into the slide tube, through

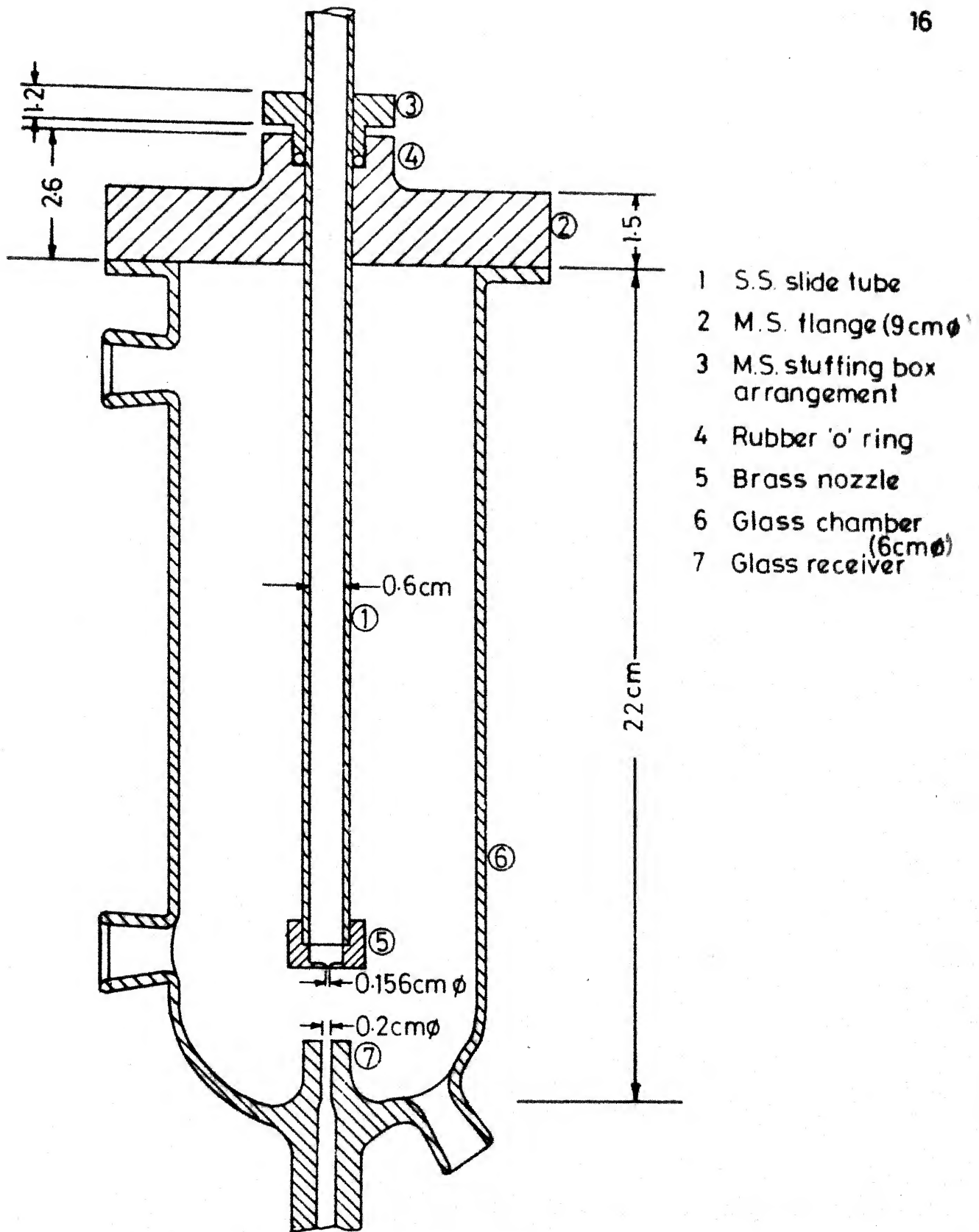


Fig 3.2 -Details of laminar jet.

a rotameter. The overhead tank was placed about 305 cm above the absorption chamber to provide sufficient head to give the required flow rate. The level in the receiver was also adjusted so that the gas entrainment with the liquid was eliminated. The jet length and diameter were measured by a travelling microscope. The absorption chamber was flushed with carbon dioxide saturated with water-vapour to purge any air in the chamber and carbon dioxide balloon was connected to the chamber keeping all other outlets closed. As the steady state condition was attained the rate of absorption of carbon dioxide was measured by soap bubble meter.

The average linear velocity of the liquid jet was varied from 79 to 370 cm/s over a distance of 0.5 to 8.5 cm to cover contact time range of 0.0025 to 0.025 s. The maximum operable jet length was limited by the instability of the moving column.

3.2 Absorbents:

The following absorbents were used for the experiments:

- (a) Distilled deaerated water
- (b) Sodium sulphide solutions (0.05 - 0.212 M Na_2S)
- (c) Sodium sulphide - sodium chloride solutions
(0.1M Na_2S + (0.5 - 5M) NaCl)
- (d) Sodium sulphide - sodium sulphate solutions
(0.1M Na_2S + (0.2 - 2M) Na_2SO_4).

3.3 Analysis:

Samples taken from the experiments were analysed for the determination of sodium sulphide content by usual acidimetric titration (Appendix A).

pH Measurements: pH value of the samples was determined using Elico Digital pH meter Model LI-120, standardized by BDH Buffer.

CHAPTER 4

RESULTS AND DISCUSSION

Experiments for the absorption of carbon dioxide in sodium sulphide solutions were conducted in laminar jet apparatus. The various systems studied in laminar jet are presented in the order of increasing complexity.

- (i) Water
- (ii) Sodium sulphide
- (iii) Sodium sulphide-sodium chloride
- (iv) Sodium sulphide-sodium sulphate

4.1 Absorption of Carbon Dioxide in Water:

The physical absorption of carbon dioxide was studied in laminar jet apparatus to verify the hydrodynamics of the jet.

The laminar jet was first calibrated by carrying out a series of experiments with absorption of carbon dioxide in distilled deaerated water at 19°C in order to estimate the diffusivity of carbon dioxide in water. For a "perfect" jet the total rate of absorption is given by equation (2.10).

$$q = 4A^* (D_A \text{ } v h)^{\frac{1}{2}} \quad (2.10)$$

A jet diameter of 1.56 mm and jet lengths of 1.6 cm and 2.0 cm were used in the experiments and equation (2.10) is plotted in Figure 4.1. The various values of liquid flow rate,

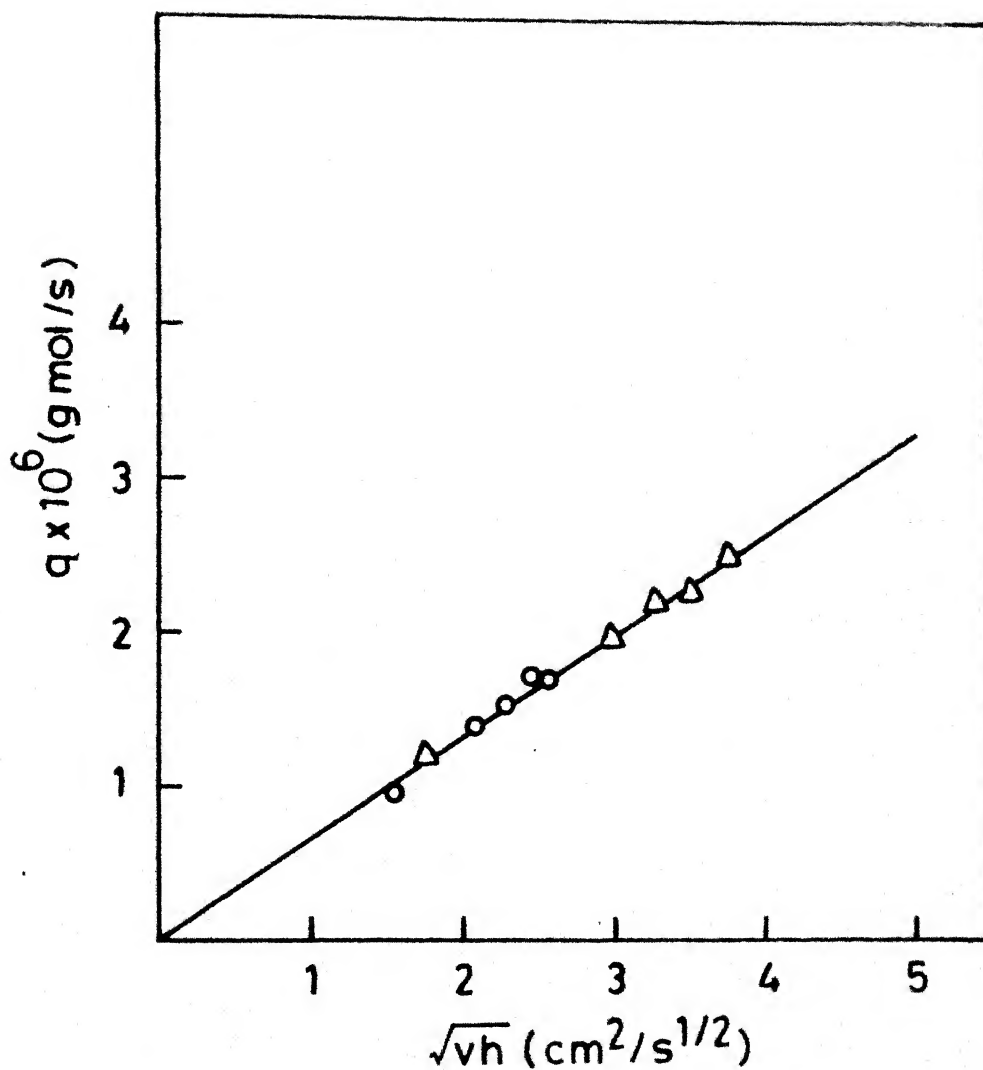


Fig.4.1 - Absorption of CO_2 into water laminar jet ; 19°C , 1 atm CO_2 .

o 1.6 cm ; Δ 2.0 cm (jet length)

v , and total absorption rate of gas, q , are tabulated in Table 4.1. From the slope of the graph the value of $A \cdot D_A^{\frac{1}{2}}$ can be calculated. The mean value of the diffusivity of carbon dioxide in water, D_A , was found to be $1.71 \times 10^{-5} \text{ cm}^2/\text{s}$ and agrees very well with the interpolated value of $1.64 \times 10^{-5} \text{ cm}^2/\text{s}$ at 19°C obtained from the data of Nijssing et al.⁽⁵⁾. This discrepancy is very small and the jet can be considered to be perfect.

4.2 Absorption of Carbon Dioxide into Sodium Sulphide Solutions:

Carbon dioxide was absorbed into laminar jets of sodium sulphide solution of concentration varied from 0.05 to 0.212 M. The experimental conditions and the calculated values of absorption rate per unit area in time t , Q , are given in Table 4.2 of Appendix B.

The experimental data are plotted in Figure 4.2 and Figure 4.3 for various sodium sulphide concentrations and temperatures.

It has been shown⁽³⁾ that for a pseudo-first order reaction, the absorption rate is given by equation (2.12)

$$Q = tA^* (D_A k_2 B^O)^{\frac{1}{2}} \quad (2.12)$$

The pseudo-first order condition for absorption into quiescent liquid is

$$(\pi k_2 B^O t/4)^{\frac{1}{2}} \ll 1 + \frac{B^O}{2A^*} \quad (4.1)$$

TABLE 4.1: ABSORPTION OF CO₂ AT 1 ATMOSPHERE PRESSURE INTO
WATER LAMINAR JET AT 19°C

| run no. | Water flow rate, $v(\text{cm}^3/\text{s})$ | Jet length, $h(\text{cm})$ | Gas flow rate $q \times 10^6 (\text{gmol/s})$ | $(vh)^{1/2}$ $(\text{cm}^2/\text{s}^{1/2})$ | $A \cdot D_A^{1/2} \times 10^8$ $(\text{gmol}/\text{cm}^2 \text{s}^{1/2})$ | $D_A \times 10^5$ (cm^2/s) |
|------------|--|----------------------------------|---|--|---|---|
| | 1.51 | 1.6 | 0.95 | 1.554 | | |
| | 2.75 | 1.6 | 1.38 | 2.097 | | |
| | 3.37 | 1.6 | 1.54 | 2.32 | | |
| | 3.742 | 1.6 | 1.73 | 2.45 | | |
| | 3.99 | 1.6 | 1.67 | 2.53 | | |
| | | | | | 16.55 | 1.71 |
| | 1.53 | 2.0 | 1.20 | 1.75 | | |
| | 4.50 | 2.0 | 1.95 | 3.00 | | |
| | 5.29 | 2.0 | 2.20 | 3.25 | | |
| | 6.12 | 2.0 | 2.25 | 3.50 | | |
| | 7.00 | 2.0 | 2.48 | 3.75 | | |

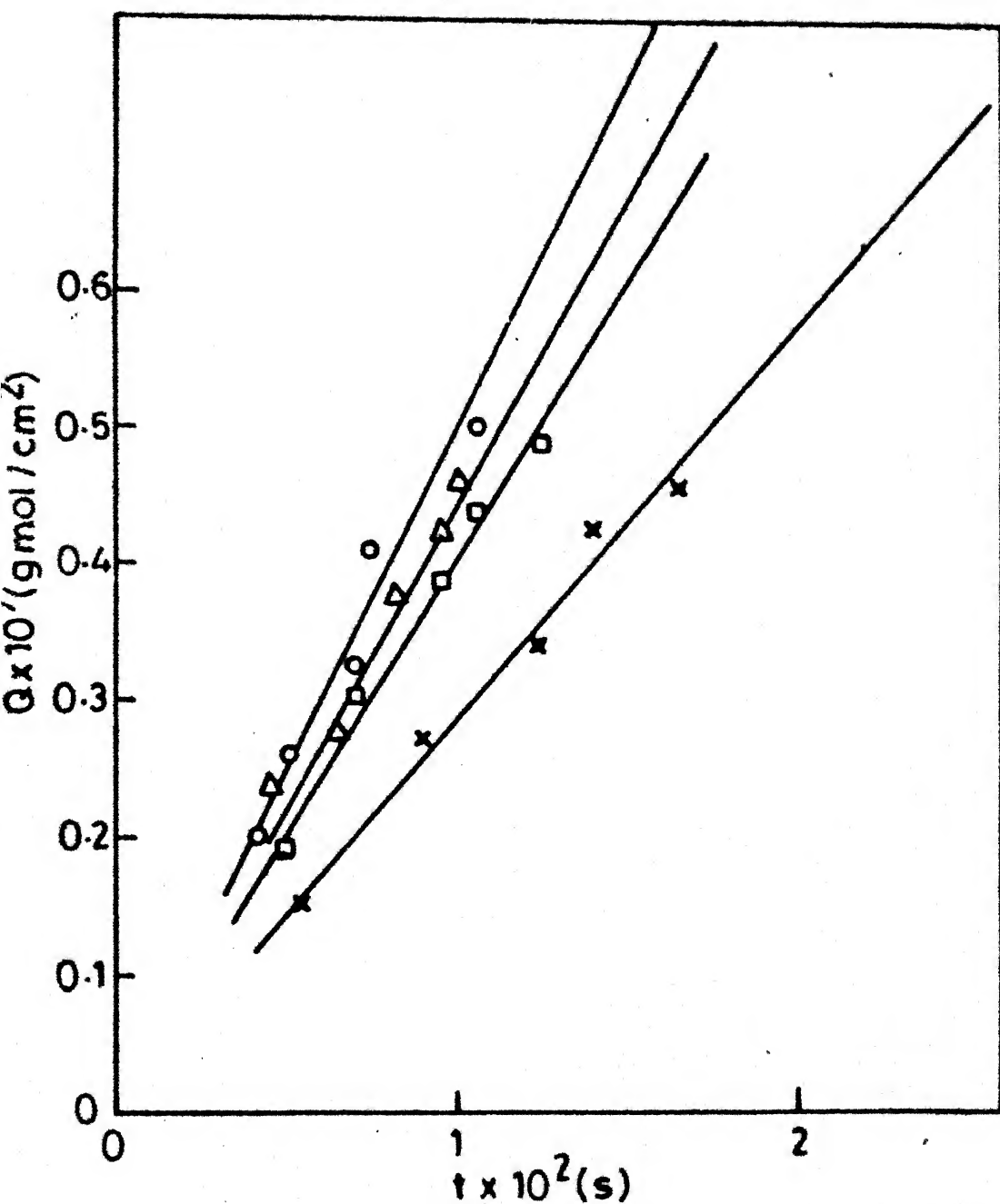


Fig.4.2 - Absorption of CO_2 into sodium sulphide solutions in laminar jet at 27°C .

\times - 0.050M- Na_2S ; \square - 0.110M- Na_2S ;

Δ - 0.151M- Na_2S ; \circ - 0.212M- Na_2S .

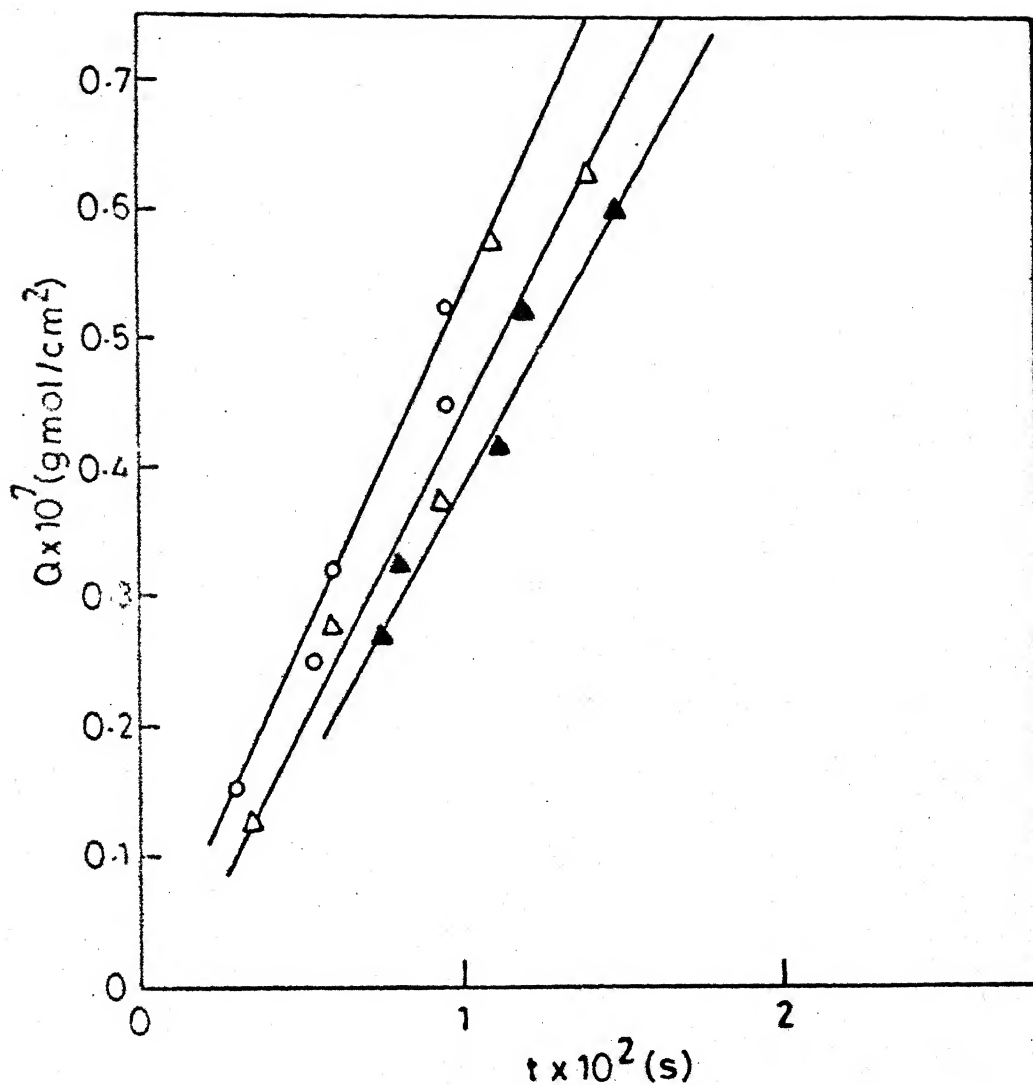


Fig. 4.3 - Absorption of CO₂ into sodium sulphide solutions in laminar jet.
 ▲ - 0.162M-Na₂S (19°C); Δ - 0.205M-Na₂S (30°C);
 ○ - 0.195M-Na₂S (32°C).

The conditions given by equation (4.1) and $k_2 B^0 t > 10$ must be satisfied in order to fit the equation (2.12) to the experimental values of absorption rate. The contact time limits were calculated for typical values of $B^0 = 0.205 \text{ M}$, $k_2 = 11000 \text{ litre/gmol s}$ and $A^* = 2.50 \times 10^{-5} \text{ gmol/cm}^3$. The upper and lower limits for contact time, t , were found as

$$0.004 < t < 0.018 \text{ s} \quad (4.2)$$

It can be seen that the experimental conditions correspond to contact times within 10% of the limit (4.2).

The rate constant, k_2 , was calculated using equation (2.12) by plotting absorption rate per unit area in time t, Q , against contact time, t , as shown in Figure 4.2 and Figure 4.3. Solubility of carbon dioxide used in the above calculations were estimated from equation (4.3)⁽³⁾.

$$\log (H/H_w) = h_1 I_1 + h_2 I_2 + \dots \quad (4.3)$$

where h_1, h_2 are solubility factor for the individual electrolytes (litre/gmol);

I_1, I_2 are the individual contributions to the ionic strength (gion/litre);

H Henry's law constant in electrolyte ($\text{atm cm}^3/\text{gmol}$);

H_w Henry's law constant in water ($\text{atm cm}^3/\text{gmol}$).

The values of H_w , the solubility of carbon dioxide in water at different temperatures are given in Table 2.2. The diffusivity of carbon dioxide in the solution was estimated

according to equation (4.4)⁽⁹⁾

$$\frac{D_A \mu}{T} = \text{Constant} \quad (4.4)$$

where D_A = diffusivity of CO_2 in solution (cm^2/s);

μ = viscosity of liquid (cp);

T = temperature ($^\circ\text{C}$)

The values of the rate constant are given in Table 4.3 for various concentrations of sodium sulphide solutions at different temperatures. Sample calculations of rate constant for typical run is given in Appendix B. The value of k_2 in sodium hydroxide solution at 30°C is 12400 litre/gmol.s and the present study value of k_2 in sodium sulphide solution at 30°C is 10950 litre/gmol.s. Thus it can be seen that the value of the rate constant, k_2 , in sodium sulphide solutions is about 11% lower than that for sodium hydroxide solutions.⁽⁶⁾

Effect of sodium sulphide concentration on the rate constant, k_2 , was studied. Figure 4.4 shows the effect of sodium sulphide concentration on the rate constant, k_2 . It can be seen from the figure that the rate constant, k_2 , is independent of the sodium sulphide concentrations.

The experimental value of enhancement factor, E , was calculated using average values of absorption rate per unit area in time t , Q , and contact time, t , according to equation (4.5).

$$E = \frac{Q}{2A^*} (\pi/D_A t)^{\frac{1}{2}} \quad (4.5)$$

TABLE 4.3: RATE CONSTANT, k_2 , FOR THE REACTION
OF CO_2 WITH HYDROXYL ION

| Na_2S (gmol/litre) | Temperature ($^{\circ}\text{C}$) | Rate constant, k_2 (litre/gmol s) |
|---------------------------------------|---------------------------------------|--|
| 0.162 | 19 | 4850 |
| 0.050 | 27 | 9031 |
| 0.110 | 27 | 9174 |
| 0.151 | 27 | 9047 |
| 0.212 | 27 | 9151 |
| 0.205 | 30 | 10950 |
| 0.195 | 32 | 12250 |

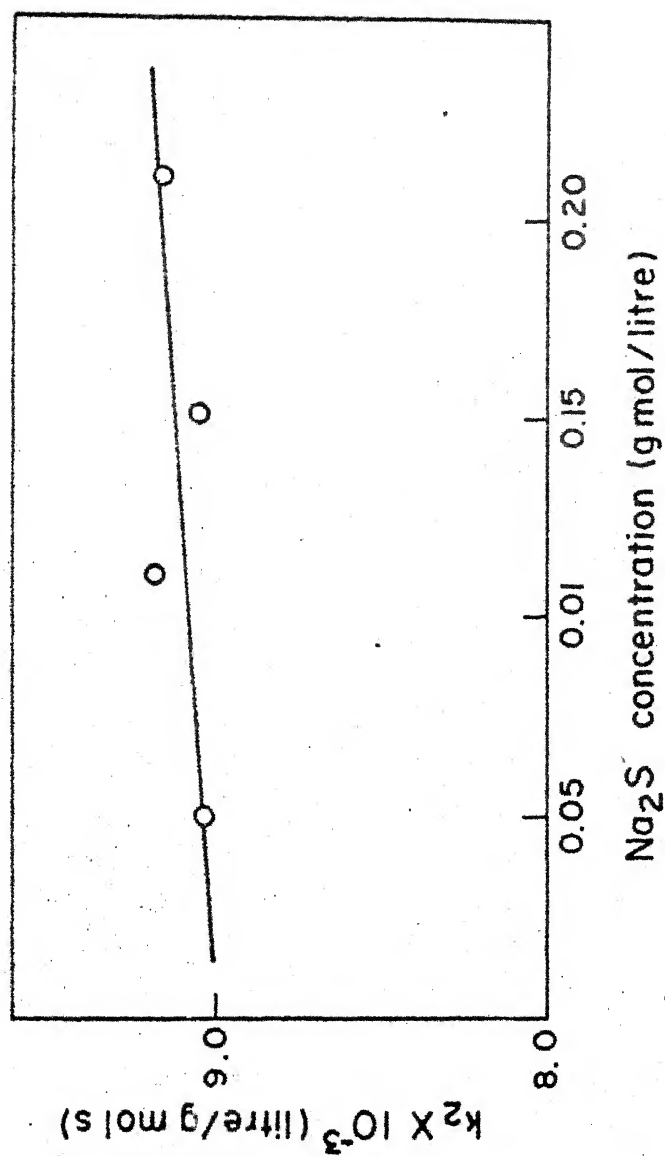


Fig. 4.4 Effect of sodium sulphide concentration on the reaction rate constant k_2

The enhancement factor, E , was calculated theoretically also using the graphs given by van Krevelen et al.⁽¹⁶⁾. The theoretical values of E were calculated using the rate constant, k_2 . Table 4.4 gives the experimental and theoretical values of enhancement factor for Na_2S solutions. The value of E is found to increase with increase in Na_2S concentration. The experimental values of E are in good agreement with the theoretical predictions.

The pH of Na_2S solutions was measured with the help of pH meter. The pH value of various sodium sulphide solutions is given in Table 4.5. The pH value increases with increase in sodium sulphide concentration because of hydrolysis of sodium sulphide into OH^- ions. Since the pH value of the solution is greater than 10, therefore reaction (2.3) is the rate controlling step. However, the change in pH value is not significant with change in sodium sulphide concentrations.

4.3 Carbon Dioxide Absorption into Sodium Sulphide - Sodium Chloride and Sodium Sulphate Solutions:

Sodium chloride and sodium sulphate were used as electrolytes to study the effect of ionic strength on the rate of absorption and rate constant. The concentration of sodium chloride and sodium sulphate was varied from 0.5 to 5.0 M. The concentration of sodium sulphide was maintained constant at 0.1 M. The experimental data and calculated

TABLE 4.4: ENHANCEMENT FACTOR FOR CO₂ ABSORPTION
IN Na₂S SOLUTIONS

Temperature = 27°C

| Na ₂ S ($\frac{\text{g mol}}{\text{litre}}$) | Enhancement factor, E | |
|--|-----------------------|-------------|
| | Experimental | Theoretical |
| 0.050 | 1.99 | 1.64 |
| 0.110 | 2.62 | 2.20 |
| 0.151 | 3.09 | 2.80 |
| 0.212 | 3.20 | 3.00 |

TABLE 4.5: pH OF SODIUM SULPHIDE SOLUTIONS

Temperature = 18°C

| Na ₂ S (gmol/litre) | pH |
|-----------------------------------|-------|
| 0.050 | 12.33 |
| 0.110 | 12.60 |
| 0.151 | 12.68 |
| 0.162 | 12.72 |
| 0.195 | 12.82 |
| 0.205 | 12.84 |
| 0.212 | 12.90 |

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values of Q are given in Table 4.6 in Appendix B. All the experimental runs were conducted at a temperature of 27°C . The rate constant, k_2 , was calculated in the similar manner as earlier discussed in Section 4.2. Figure 4.5 shows the effect of addition of sodium chloride and sodium sulphate in sodium sulphide solutions. The plot shows that the rate constant, k_2 , increases linearly with increase in ionic strength (concentration of NaCl and Na_2SO_4). The results also show that the slope of the curve (Figure 4.5) is dependent upon the nature of electrolytes. The values of k_2 obtained with NaCl are higher compared to the values obtained with sodium sulphate. This may be attributed due to the strong ionic effect of NaCl compared with Na_2SO_4 .

The relation between ionic strength and rate constant, k_2 , is given as

$$\log k_2 = 3.98 + 0.128I \quad (4.6)$$

$$\log k_2 = 3.94 + 0.09 I \quad (4.7)$$

The above relations agree very well with the empirical relation reported by Pinsent et al.⁽⁶⁾ at 20°C .

$$\log k_2 = 3.77 + 0.26 I \quad (4.8)$$

The experimental and theoretical values of enhancement factor, E , were calculated in the similar manner as earlier discussed in Section 4.2. Figure 4.6 shows the effect of ionic strength on enhancement factor, E . It is found that

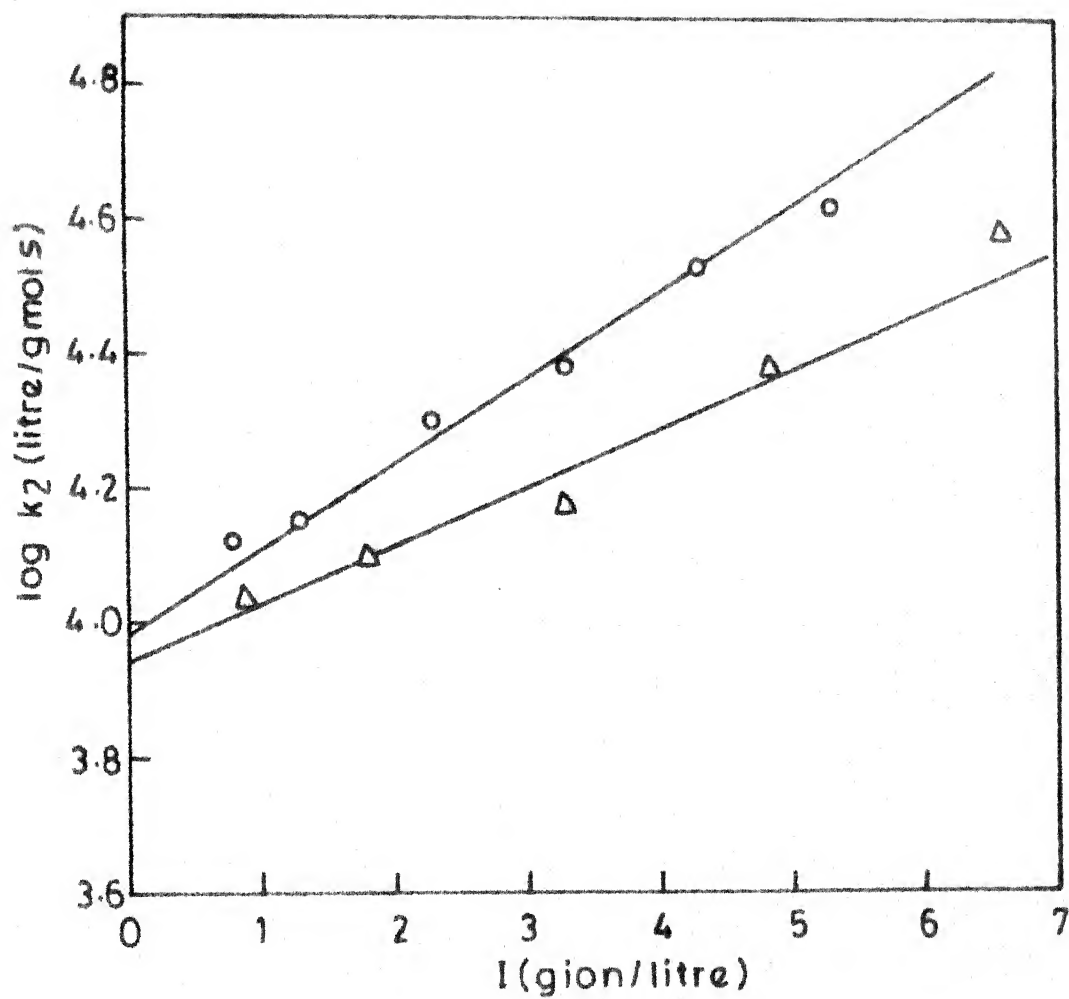


Fig. 4.5- Effect of ionic strength on the reaction rate constant k_2 .

o NaCl ; Δ Na_2SO_4 .

the values of enhancement factor increase with increase in ionic strength of the solutions. The values of enhancement factor, E , for $\text{Na}_2\text{S} - \text{NaCl}$ solutions are higher than that for $\text{Na}_2\text{S}-\text{Na}_2\text{SO}_4$. This may be due to the strong ionic effect of NaCl compared to Na_2SO_4 because NaCl being a stronger electrolyte. Furthermore, the agreement between the theoretically calculated values of E and the experimental values is good, as can be seen from Figure 4.6.

4.4 Effect of Temperature on the Kinetic Constant, k_2 :

The reaction rate constant, k_2 was determined at various temperatures to study the effect of temperature on rate constant, k_2 . The rate constant, k_2 , is found to increase with an increase in the temperature. The reaction temperature was varied over the range of 19 to 32°C. Figure 4.7 gives an Arrhenius plot of the reaction where $\log k_2$ is plotted against reciprocal of temperature. The slope of the curve gives the value of apparent activation energy of the reaction. For the purpose of comparison, data obtained by Mahagaonkar et al.⁽²⁾ and Pinsent et al.⁽⁶⁾ (thermal method) are also plotted. It is interesting to note that the rate constant values lie near the same line. The rate constant, k_2 , is related with temperature, T by equation (4.9).

$$\log k_2 = 13.045 - \frac{2730}{T} \quad (4.9)$$

where k_2 = second order rate constant (litre/gmol s)

and T = temperature (°K)

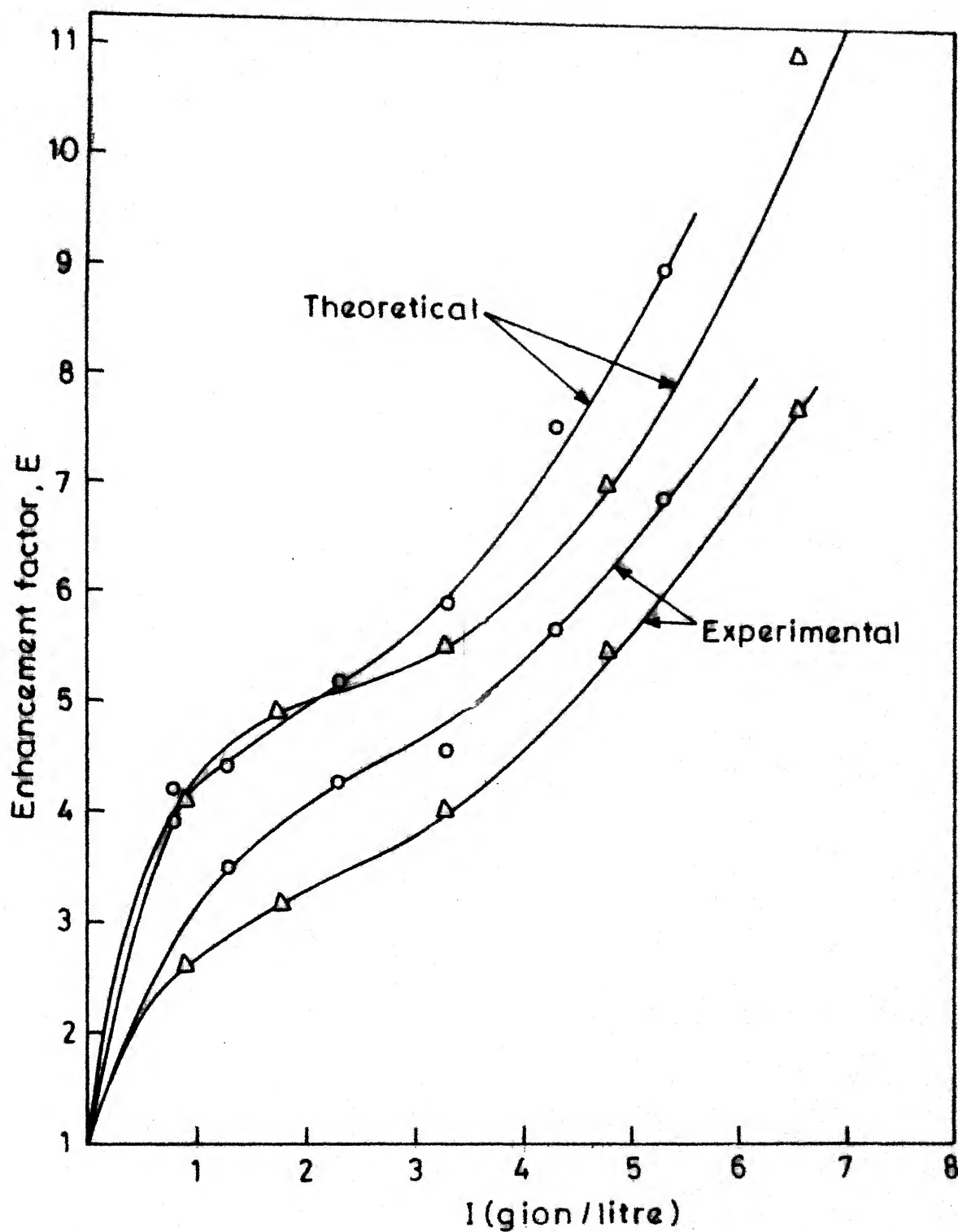


Fig. 4.6 - Enhancement factor, E vs. ionic strength I .
 \circ $\text{Na}_2\text{S} + \text{NaCl}$; Δ $\text{Na}_2\text{S} + \text{Na}_2\text{SO}_4$; $T = 27^\circ\text{C}$.

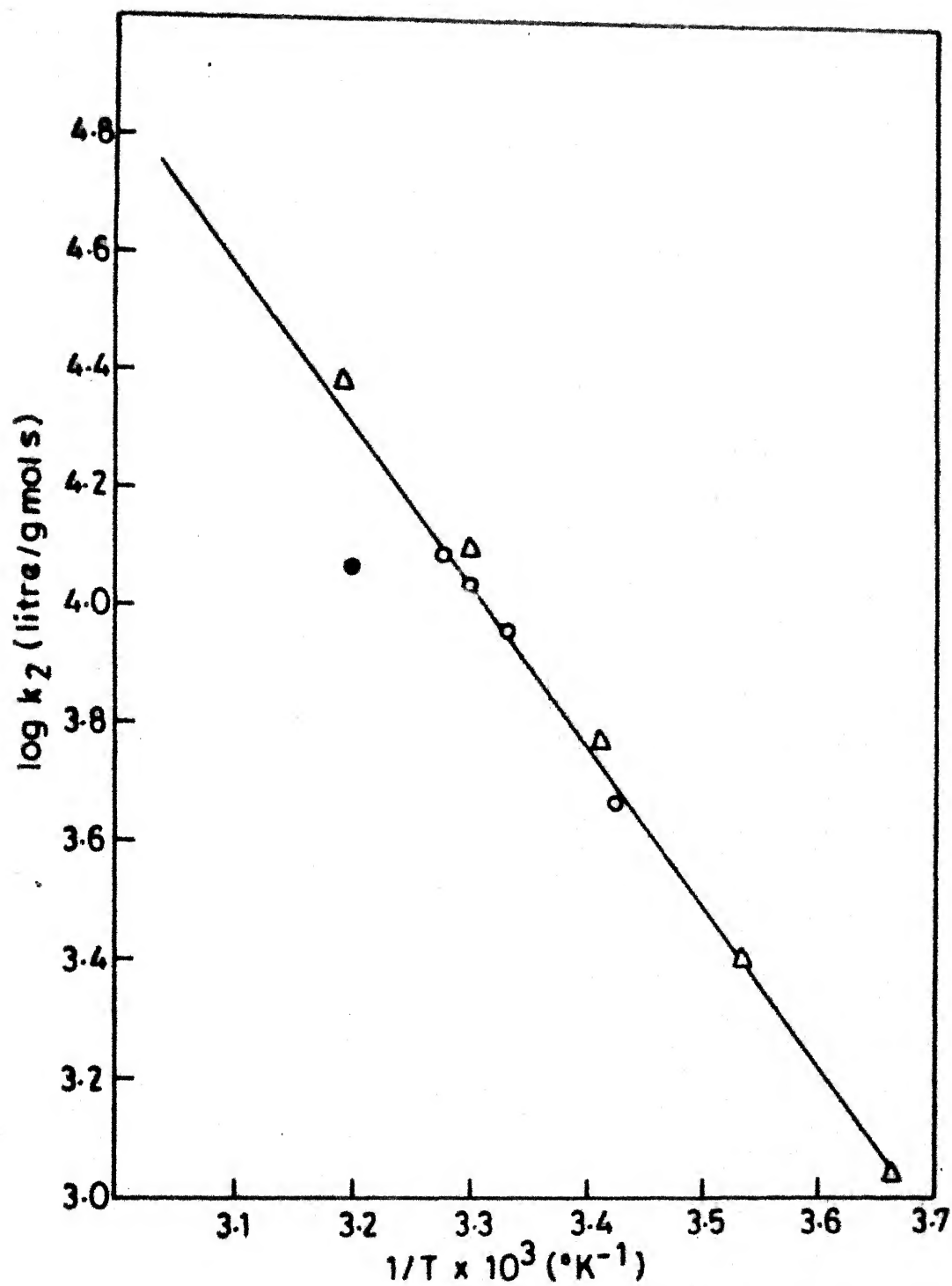


Fig. 4.7 -Effect of temperature on rate constant.

○ Present study ; Δ Pinsent et al. results ;

● Mahagaonkar et al. results.

The activation energy of the reaction was found from the slope of the curve and of the order of 12.572 kcal/gmol. This value is close to the value of 13.250 kcal/gmol reported for sodium hydroxide solutions.⁽⁶⁾

4.5 Conclusions:

To sum up the discussion of the results the following points can be made:

1. The absorption rate of carbon dioxide in sodium sulphide solutions increases with increase in the concentration of sodium sulphide. The kinetic constant, k_2 , is found to be dependent of change in the sodium sulphide concentration at a given temperature.
2. The value of rate constant, k_2 , is found to be dependent on the nature of electrolytes and their ionic strengths.

CHAPTER 5

SUMMARY AND RECOMMENDATION

The reaction of dissolved carbon dioxide with hydroxyl ions is modelled as pseudo-first order reaction in laminar jet apparatus. The kinetic constant, k_2 , depends upon ionic strength, nature of electrolyte, temperature and sodium sulphide concentration. The value of k_2 obtained in the present study for sodium sulphide solutions is compared with reported values (found with different methods). The value of k_2 is however, lower than that of sodium hydroxide solution by about 11 per-cent.⁽⁶⁾

The rate constant value obtained in the present study will be useful for the design of gas-liquid contacting equipment.

The technique demonstrated in this study can be extended for investigating carbonation of the complex black liquors, where organic constituents like lignin also play a significant role.

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APPENDIX AANALYSIS

The method⁽¹⁷⁾ used for analysing the experimental samples, is outlined below.

A 5 cc portion of the sample is pipetted into a flask. About 25 cc of 10 per cent BaCl_2 solution are added with a few drops of phenolphthalien indicator and the solution is titrated with 0.526N HCl until the pink colour disappears. The burette reading is recorded as A. The burette is not refilled. 5 cc of 40 per cent formaldehyde solution are added to the flask. The pink colour returns and after a minute titration is continued until the pink colour again disappears. The burette reading is recorded as B. The molar concentration of sodium sulphide in the samples are calculated from

$$\text{Na}_2\text{S} = 2(\text{B}-\text{A}) \quad \text{gmol/litre}$$

APPENDIX B

TABLES OF EXPERIMENTAL DATA AND SAMPLE
CALCULATIONS

TABLE 4.2: DATA FOR ABSORPTION OF CARBON DIOXIDE AT 1 ATMOSPHERE PRESSURE IN LAMINAR JET
OF SODIUM SULPHIDE SOLUTIONS

| Run No. | Temperature (°C) | Liquid Flow Rate v (cm ³ /s) | Jet Length h (cm) | Gas Flow Rate $q \times 10^6$ (gmol/s) | Viscosity (cp) | $D_A \times 10^5$ (cm ² /s) | $A^* \times 10^5$ (gmol/cm ³) | $Q \times 10^7$ (gmol/cm ²) | Time t (s) | k_2 (litre/gmol s) |
|-------------------|------------------|---|---------------------|--|----------------|--|---|---|--------------|----------------------|
| (1) | (2) | (3) | (4) | (5) | (6) | (7) | (8) | (9) | (10) | (11) |
| $Na_2S = 0.162 M$ | | | | | | | | | | |
| 3 | 19 | 2.80 | 1.10 | 1.938 | 1.142 | 1.497 | 3.67 | 0.270 | 0.0075 | |
| | 19 | 3.77 | 1.60 | 3.141 | 1.142 | 1.497 | 3.67 | 0.325 | 0.0081 | |
| | 19 | 4.26 | 2.50 | 4.533 | 1.142 | 1.497 | 3.67 | 0.415 | 0.0112 | 4850 |
| | 19 | 4.94 | 3.10 | 6.586 | 1.142 | 1.497 | 3.67 | 0.520 | 0.0120 | |
| | 19 | 5.48 | 4.30 | 9.555 | 1.142 | 1.497 | 3.67 | 0.680 | 0.0150 | |
| $Na_2S = 0.05 M$ | | | | | | | | | | |
| 4 | 27 | 3.00 | 0.88 | 1.154 | 0.910 | 1.980 | 3.06 | 0.150 | 0.0055 | |
| | 27 | 3.80 | 1.80 | 2.680 | 0.910 | 1.980 | 3.06 | 0.275 | 0.0090 | |
| | 27 | 4.60 | 3.00 | 3.950 | 0.910 | 1.980 | 3.06 | 0.335 | 0.0124 | 9031 |
| | 27 | 5.60 | 4.10 | 6.100 | 0.910 | 1.980 | 3.06 | 0.425 | 0.0140 | |
| | 27 | 6.40 | 5.50 | 7.460 | 0.910 | 1.980 | 3.06 | 0.455 | 0.0165 | |
| $Na_2S = 0.11 M$ | | | | | | | | | | |
| 5 | 27 | 2.10 | 0.55 | 1.023 | 0.950 | 1.868 | 2.96 | 0.190 | 0.0050 | |
| | 27 | 4.20 | 2.00 | 3.200 | 0.950 | 1.868 | 2.96 | 0.300 | 0.0070 | |
| | 27 | 5.17 | 2.60 | 4.984 | 0.950 | 1.868 | 2.96 | 0.376 | 0.0096 | 9174 |
| | 27 | 5.80 | 3.20 | 6.395 | 0.950 | 1.868 | 2.96 | 0.430 | 0.0105 | |
| | 27 | 6.10 | 4.00 | 7.660 | 0.950 | 1.868 | 2.96 | 0.490 | 0.0125 | 43 |

| (2) | (3) | (4) | (5) | (6) | (7) | (8) | (9) | (10) | (11) |
|---|------|------|-------|-------|-------|------|-------|--------|-------|
| $\text{Na}_2\text{S} = 0.15 \text{ M}$ | | | | | | | | | |
| 27 | 3.32 | 0.80 | 2.100 | 0.985 | 1.801 | 2.87 | 0.260 | 0.0046 | |
| 27 | 3.67 | 1.25 | 3.293 | 0.985 | 1.801 | 2.87 | 0.350 | 0.0065 | |
| 27 | 4.70 | 2.00 | 4.519 | 0.985 | 1.801 | 2.87 | 0.375 | 0.0081 | 9047 |
| 27 | 5.00 | 2.50 | 5.450 | 0.985 | 1.801 | 2.87 | 0.425 | 0.0095 | |
| 27 | 5.70 | 3.00 | 6.723 | 0.985 | 1.801 | 2.87 | 0.460 | 0.0100 | |
| $\text{Na}_2\text{S} = 0.212 \text{ M}$ | | | | | | | | | |
| 27 | 4.10 | 0.90 | 2.100 | 1.050 | 1.690 | 2.79 | 0.200 | 0.0042 | |
| 27 | 4.50 | 1.20 | 2.900 | 1.050 | 1.690 | 2.79 | 0.251 | 0.0051 | |
| 27 | 5.46 | 2.00 | 4.914 | 1.050 | 1.690 | 2.79 | 0.351 | 0.0070 | 9151 |
| 27 | 6.40 | 2.50 | 6.728 | 1.050 | 1.690 | 2.79 | 0.410 | 0.0075 | |
| 27 | 6.85 | 3.80 | 8.870 | 1.050 | 1.690 | 2.79 | 0.505 | 0.0106 | |
| $\text{Na}_2\text{S} = 0.205 \text{ M}$ | | | | | | | | | |
| 30 | 3.60 | 0.66 | 1.150 | 0.925 | 1.970 | 2.50 | 0.125 | 0.0035 | |
| 30 | 4.40 | 1.38 | 2.250 | 0.925 | 1.970 | 2.50 | 0.280 | 0.0061 | |
| 30 | 4.90 | 2.43 | 4.710 | 0.925 | 1.970 | 2.50 | 0.375 | 0.0095 | 10950 |
| 30 | 5.40 | 3.10 | 7.960 | 0.925 | 1.970 | 2.50 | 0.575 | 0.0110 | |
| 30 | 5.90 | 5.86 | 9.450 | 0.925 | 1.970 | 2.50 | 0.625 | 0.0190 | |
| $\text{Na}_2\text{S} = 0.195 \text{ M}$ | | | | | | | | | |
| 32 | 3.20 | 0.50 | 1.230 | 0.905 | 1.987 | 2.42 | 0.150 | 0.0030 | |
| 32 | 3.80 | 1.09 | 2.436 | 0.905 | 1.987 | 2.42 | 0.250 | 0.0055 | |
| 32 | 4.50 | 1.41 | 3.704 | 0.905 | 1.987 | 2.42 | 0.321 | 0.0060 | 12250 |
| 32 | 5.20 | 2.61 | 6.000 | 0.905 | 1.987 | 2.42 | 0.450 | 0.0096 | |
| 32 | 6.00 | 3.07 | 8.077 | 0.905 | 1.987 | 2.42 | 0.525 | 0.0098 | |

TABLE 4.6: DATA FOR ABSORPTION OF CARBON DIOXIDE AT 1 ATMOSPHERE PRESSURE IN LAMINAR JET OF SODIUM SULPHIDE SOLUTIONS CONTAINING ELECTROLYTES

| Run No. | Temperature (°C) | Liquid Flow Rate v (cm ³ /s) | Jet Length h (cm) | Gas Flow Rate $q \times 10^6$ (gmol/s) | Viscosity (cp) | $D_A \times 10^5$ (cm ² /s) | $A^* \times 10^3$ (gmol/cm ³) | $Q \times 10^7$ (gmol/cm ²) | Time t (s) | k_2 (litre/gmol) |
|--|------------------|---|---------------------|--|----------------|--|---|---|--------------|--------------------|
| (1) | (2) | (3) | (4) | (5) | (6) | (7) | (8) | (9) | (10) | (11) |
| Na₂S = 0.1 M; NaCl = 0.5 M; I = 0.8 gion/litre | | | | | | | | | | |
| 10 | 27 | 3.35 | 0.72 | 2.147 | 1.040 | 1.7325 | 2.66 | 0.250 | 0.0041 | |
| | 27 | 3.42 | 1.34 | 3.064 | 1.040 | 1.7325 | 2.66 | 0.350 | 0.0075 | |
| | 27 | 4.98 | 2.28 | 5.746 | 1.040 | 1.7325 | 2.66 | 0.450 | 0.0088 | 12916 |
| | 27 | 5.46 | 3.00 | 8.540 | 1.040 | 1.7325 | 2.66 | 0.500 | 0.0105 | |
| | 27 | 6.69 | 4.20 | 10.460 | 1.040 | 1.7325 | 2.66 | 0.610 | 0.0120 | |
| | 27 | 7.06 | 4.80 | 11.310 | 1.040 | 1.7325 | 2.66 | 0.620 | 0.0130 | |
| Na₂S = 0.1M; NaCl = 1.0 M; I = 1.3 gion/litre | | | | | | | | | | |
| 11 | 27 | 2.80 | 0.66 | 1.077 | 1.150 | 1.5668 | 2.40 | 0.150 | 0.0045 | |
| | 27 | 3.50 | 1.10 | 2.378 | 1.150 | 1.5668 | 2.40 | 0.265 | 0.0060 | |
| | 27 | 4.60 | 2.41 | 4.246 | 1.150 | 1.5668 | 2.40 | 0.360 | 0.0100 | 14288 |
| | 27 | 5.20 | 3.14 | 6.330 | 1.150 | 1.5668 | 2.40 | 0.475 | 0.0115 | |
| | 27 | 5.00 | 3.67 | 7.200 | 1.150 | 1.5668 | 2.40 | 0.540 | 0.0140 | |
| Na₂S = 0.1 M; NaCl = 2.0 M; I = 2.3 gion/litre | | | | | | | | | | |
| 12 | 27 | 3.41 | 0.75 | 1.093 | 1.195 | 1.5070 | 1.942 | 0.125 | 0.0042 | |
| | 27 | 3.75 | 1.59 | 2.403 | 1.195 | 1.5070 | 1.942 | 0.250 | 0.0081 | |
| | 27 | 4.50 | 2.59 | 4.615 | 1.195 | 1.5070 | 1.942 | 0.400 | 0.0110 | 19749 |
| | 27 | 5.00 | 3.94 | 6.410 | 1.195 | 1.5070 | 1.942 | 0.500 | 0.0150 | |
| | 27 | 6.00 | 4.89 | 8.846 | 1.195 | 1.5070 | 1.942 | 0.575 | 0.0155 | 45 |

Table 4.6 contd

| (1) | (2) | (3) | (4) | (5) | (6) | (7) | (8) | (9) | (10) | (11) |
|---|-----|------|------|-------|-------|--------|-------|-------|--------|-------|
| $\text{Na}_2\text{S} = 0.1 \text{ M}$, $\text{NaCl} = 3.0 \text{ M}$, $I = 3.3 \text{ gion/litre}$ | | | | | | | | | | |
| 13 | 27 | 2.55 | 0.80 | 0.837 | 1.310 | 1.3700 | 1.572 | 0.128 | 0.0060 | |
| | 27 | 3.11 | 1.14 | 1.595 | 1.310 | 1.3700 | 1.572 | 0.200 | 0.0070 | 24118 |
| | 27 | 3.46 | 1.90 | 2.660 | 1.310 | 1.3700 | 1.572 | 0.300 | 0.0105 | |
| | 27 | 4.55 | 3.10 | 4.960 | 1.310 | 1.3700 | 1.572 | 0.425 | 0.0130 | |
| | 27 | 5.50 | 4.50 | 6.760 | 1.310 | 1.3700 | 1.572 | 0.475 | 0.0155 | |
| $\text{Na}_2\text{S} = 0.1 \text{ M}$, $\text{NaCl} = 4.0 \text{ M}$, $I = 4.3 \text{ gion/litre}$ | | | | | | | | | | |
| 14 | 27 | 2.32 | 0.85 | 0.823 | 1.450 | 1.2400 | 1.270 | 0.150 | 0.0070 | |
| | 27 | 4.18 | 1.75 | 0.950 | 1.450 | 1.2400 | 1.270 | 0.275 | 0.0080 | |
| | 27 | 4.58 | 3.20 | 4.060 | 1.450 | 1.2400 | 1.270 | 0.350 | 0.0135 | 33802 |
| | 27 | 5.70 | 4.17 | 5.773 | 1.450 | 1.2400 | 1.270 | 0.395 | 0.0140 | |
| | 27 | 6.66 | 5.58 | 7.600 | 1.450 | 1.2400 | 1.270 | 0.445 | 0.0160 | |
| $\text{Na}_2\text{S} = 0.1 \text{ M}$, $\text{NaCl} = 5.0 \text{ M}$, $I = 5.3 \text{ gion/litre}$ | | | | | | | | | | |
| 15 | 27 | 2.40 | 1.00 | 1.077 | 1.510 | 1.1900 | 1.030 | 0.175 | 0.0080 | |
| | 27 | 2.90 | 1.75 | 1.866 | 1.510 | 1.1900 | 1.030 | 0.250 | 0.0115 | |
| | 27 | 3.62 | 2.50 | 3.016 | 1.510 | 1.1900 | 1.030 | 0.325 | 0.0132 | 41923 |
| | 27 | 4.34 | 3.75 | 4.340 | 1.510 | 1.1900 | 1.030 | 0.390 | 0.0165 | |
| | 27 | 5.13 | 5.10 | 6.180 | 1.510 | 1.1900 | 1.030 | 0.470 | 0.0190 | |
| $\text{Na}_2\text{S} = 0.1 \text{ M}$, $\text{Na}_2\text{SO}_4 = 0.2 \text{ M}$, $I = 0.9 \text{ gion/litre}$ | | | | | | | | | | |
| 16 | 27 | 2.90 | 0.76 | 1.308 | 0.980 | 1.8400 | 2.600 | 0.176 | 0.0050 | |
| | 27 | 3.40 | 1.24 | 2.048 | 0.980 | 1.8400 | 2.600 | 0.235 | 0.0070 | |
| | 27 | 4.20 | 1.76 | 3.230 | 0.980 | 1.8400 | 2.600 | 0.300 | 0.0080 | 10828 |
| | 27 | 5.50 | 3.30 | 5.640 | 0.980 | 1.8400 | 2.600 | 0.400 | 0.0115 | |
| | 27 | 6.10 | 4.00 | 6.491 | 0.980 | 1.8400 | 2.600 | 0.415 | 0.0125 | |

Table 4.6 contd.

| | (1) | (2) | (3) | (4) | (5) | (6) | (7) | (8) | (9) | (10) | (11) |
|----|-----|-----|---|------|-------|-------|--------|-------|-------|--------|-------|
| | | | $\text{Na}_2\text{S} = 0.1 \text{ M}; \text{Na}_2\text{SO}_4 = 0.5 \text{ M}, I = 1.8 \text{ gion/litre}$ | | | | | | | | |
| 18 | 7 | 27 | 2.60 | 0.54 | 0.660 | 1.215 | 1.4830 | 2.150 | 0.100 | 0.0040 | |
| | 27 | 27 | 4.20 | 1.31 | 2.153 | 1.215 | 1.4830 | 2.150 | 0.200 | 0.0060 | |
| | 27 | 27 | 4.90 | 2.60 | 2.950 | 1.215 | 1.4830 | 2.150 | 0.310 | 0.0101 | 12449 |
| | 27 | 27 | 5.40 | 3.51 | 5.384 | 1.215 | 1.4830 | 2.150 | 0.375 | 0.0120 | |
| | 27 | 27 | 6.40 | 4.85 | 7.138 | 1.215 | 1.4830 | 2.150 | 0.435 | 0.0145 | |
| | | | $\text{Na}_2\text{S} = 0.1 \text{ M}; \text{Na}_2\text{SO}_4 = 1.0 \text{ M}; I = 3.3 \text{ gion/litre}$ | | | | | | | | |
| | 27 | 27 | 3.50 | 1.10 | 1.346 | 1.250 | 1.4410 | 1.560 | 0.150 | 0.0060 | |
| | 27 | 27 | 3.95 | 1.80 | 2.278 | 1.250 | 1.4410 | 1.560 | 0.225 | 0.0088 | |
| | 27 | 27 | 4.50 | 2.70 | 3.173 | 1.350 | 1.4410 | 1.560 | 0.275 | 0.0115 | 14947 |
| | 27 | 27 | 5.20 | 3.26 | 4.733 | 1.250 | 1.4410 | 1.560 | 0.355 | 0.0130 | |
| | 27 | 27 | 6.40 | 4.85 | 6.810 | 1.250 | 1.4410 | 1.560 | 0.415 | 0.0165 | |
| | | | $\text{Na}_2\text{S} = 0.1 \text{ M}; \text{Na}_2\text{SO}_4 = 1.5 \text{ M}; I = 4.8 \text{ gion/litre}$ | | | | | | | | |
| 19 | 27 | 27 | 2.90 | 0.93 | 0.892 | 1.310 | 1.3750 | 1.130 | 0.120 | 0.0061 | |
| | 27 | 27 | 3.80 | 2.00 | 2.000 | 1.310 | 1.3750 | 1.130 | 0.205 | 0.0100 | |
| | 27 | 27 | 4.40 | 3.22 | 3.680 | 1.310 | 1.3750 | 1.130 | 0.325 | 0.0140 | 23399 |
| | 27 | 27 | 5.40 | 5.65 | 5.880 | 1.310 | 1.3750 | 1.130 | 0.425 | 0.0200 | |
| | 27 | 27 | 6.60 | 7.42 | 8.038 | 1.310 | 1.3750 | 1.130 | 0.475 | 0.0215 | |
| | | | $\text{Na}_2\text{S} = 0.1 \text{ M}; \text{Na}_2\text{SO}_4 = 2.0 \text{ M}; I = 6.6 \text{ gion/litre}$ | | | | | | | | |
| 20 | 27 | 27 | 2.20 | 1.09 | 0.902 | 1.381 | 1.3040 | 0.770 | 0.160 | 0.0095 | |
| | 27 | 27 | 3.50 | 2.47 | 2.240 | 1.381 | 1.3040 | 0.770 | 0.250 | 0.0135 | |
| | 27 | 27 | 4.30 | 4.50 | 3.860 | 1.381 | 1.3040 | 0.770 | 0.350 | 0.0200 | 38327 |
| | 27 | 27 | 5.20 | 5.57 | 5.330 | 1.381 | 1.3040 | 0.770 | 0.400 | 0.0205 | |
| | 27 | 27 | 6.50 | 8.50 | 7.500 | 1.381 | 1.3040 | 0.770 | 0.455 | 0.0250 | |

SAMPLE CALCULATIONSFor Run No.4

$$B^{\circ} = 0.05 \text{ M}; T = 27^{\circ}\text{C}; v = 3.0 \text{ cm}^3/\text{s}; h = 0.88 \text{ cm};$$

$$q = 1.154 \times 10^{-6} \text{ gmol/s}; \mu = 0.91 \text{ cp}; \mu_w = 0.858 \text{ cp}^{(18)}$$

$$D_A = 2.10 \text{ cm}^2/\text{s} \text{ for } \text{CO}_2 \text{ in water (Table 2.2)}$$

Contact time is estimated by equation

$$t = \frac{\pi d^2 h}{4v} \quad (2.6)$$

$$= \frac{\pi \times (0.156)^2 \times 0.88}{4 \times 3.0} = 0.0056 \text{ s}$$

Similarly other values are estimated.

Amount of gas absorbed per unit area in contact time, t is calculated by equation

$$Q = \frac{qd}{4v} \quad (2.9)$$

$$= \frac{1.154 \times 10^{-6} \times 0.156}{4 \times 3.0}$$

$$= 0.15 \times 10^{-7} \text{ gmol/cm}^2$$

Other values are calculated in the similar manner.

Solubility of CO_2 in the solution is calculated by equation

$$\log (H/H_w) = h_1 I_1 + h_2 I_2 + \dots \quad (4.3)$$

$$h_1 = (0.091 + 0.022 - 0.0202)^{(3)}$$

$$= 0.0928 \text{ litre/gion}$$

$$I_1 = \frac{1}{2}(2+4) \times 0.05 = 0.15 \text{ gion/litre}$$

$$H_w = 0.0316 \text{ gmol/litre (Table 2.2)}$$

$$= 3.16 \times 10^{-5} \text{ gmol/cm}^3$$

Therefore $\log(0.0316 H) = 0.0928 \times 0.15$

Therefore $A^* = \frac{1}{H} = \frac{0.0316}{10^{0.013292}}$
 $= 0.0306 \text{ gmol/litre}$

Diffusivity of CO_2 in the solution is calculated by equation

$$\frac{D_A \mu}{T} = \frac{D_A \mu_w}{T} = \dots = \text{constant} \quad (4.4)$$

Therefore $D_A = \frac{D_A \mu_w}{\mu} = \frac{2.10 \times 0.858 \times 10^{-5}}{0.91}$
 $= 1.98 \times 10^{-5} \text{ cm}^2/\text{s}$

Therefore $A^* D_A^{\frac{1}{2}} = 3.06 \times 10^{-8} \times (19.8)^{\frac{1}{2}}$
 $= 13.6 \times 10^{-8} \text{ gmol/cm}^2 \text{ s}^{\frac{1}{2}}$

Rate constant k_2 is calculated by equation (2.12) using the Q vs t plot

$$Q = t A^* (D_A k_2 B^0)^{\frac{1}{2}} \quad (2.12)$$

From figure 4.2, we have

$$A^* (D_A k_2 B^0)^{\frac{1}{2}} = 0.289 \times 10^{-5}$$

Therefore $k_2 = \left(\frac{0.289 \times 10^{-5}}{13.6 \times 10^{-8}} \right)^2 \times \frac{1}{0.05}$
 $= 9031 \text{ litre/gmol s}$

Similarly other values of k_2 can be calculated.

Enhancement factor is calculated by equation

$$E = \frac{Q}{2A^*} (\pi / D_A t)^{\frac{1}{2}} \quad (4.5)$$

$$= \frac{0.328 \times 10^{-7}}{2 \times 3.06 \times 10^{-5}} (\pi / 1.98 \times 10^{-5} \times 0.01148)^{\frac{1}{2}}$$

$$= 1.99 \text{ (Experimental)}$$

Theoretical value of enhancement factor is calculated by using the graph given by van Krevelen et al. (16)

$$E = 1.64 \text{ (Theoretical)}$$